Hazard Information to Consider when Labeling of Diphenylmethane Diisocyanate (MDI), polymeric MDI and Isocyanate-terminated MDI prepolymers Containing Products for the Consumer Marketplace

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Introduction

This document provides information about the potential hazards from exposure to diphenylmethane diisocyanate (MDI), polymeric MDI (PMDI) and Isocyanate-terminated MDI prepolymers. This information is intended to assist company label writers who are responsible for communicating the potential hazards and safe handling guidelines for consumer products to prospective customers, also known as Do-It-Yourself (DIY) users. By providing this information, the Center for the Polyurethanes Industry (CPI) of the American Chemistry Council (ACC) is not recommending or endorsing the use of MDI for any specific purpose or in any particular products or categories of products. It is the responsibility of the manufacturer of each product that contains MDI to determine that the product is safe for its intended use, and to ensure that appropriate warnings and instructions are provided. The hazard information contained in this document may help companies. Additional information also is available from the MDI supplier (e.g. the (Material) Safety Data Sheet (SDS)) and on the CPI website at www.polyurethane.org.

MDI may pose serious health hazards if not used/handled properly or if repeated uncontrolled exposures occur. This document does not address products containing MDI that are intended to be heated, sprayed or otherwise applied in a manner that may generate airborne MDI. The use canister application of an insulating foam sealant (i.e., one-component foam) is not considered a spray application.

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Labeling Laws and Regulations

This document only addresses MDI, polymeric MDI and isocyanate-terminated MDI prepolymers. Under applicable laws, labels for certain hazardous substances must address the hazards of the product itself, including any synergistic or antagonistic effects among the mixture ingredients, not just the hazards of the individual components. Thus, producers of MDI-containing products must consider the hazards of the product as a whole, including all its ingredients and not just the hazards of MDI by itself.

The vast majority of MDI uses are for industrial applications. Hazard communication training, medical surveillance, training in proper handling precautions and use of personal protective equipment (PPE) are generally provided consistent with legal requirements and safe handling practices.

However, there are some MDI-containing products available to the general public, for purchase at retail stores or on-line, which can be used in DIY applications. Consumers using these products need to understand and follow appropriate safe handling practices, which may include use of Personal Protective Equipment (PPE). End-use product labels are one means of communicating this information to the DIY user and may be required under applicable laws and U.S. Consumer Product Safety Commission (CPSC) regulations.

Products that are hazardous and available for consumers to purchase or use are subject to the labeling requirements of the Federal Hazardous Substances Act (FHSA) (15 U.S.C. Section 1261), which is administered by the CPSC. These requirements are mandatory, and failure to comply with them can result in civil and/or criminal penalties. These regulations are found in the Code of Federal Regulations at 16 C.F.R. Part 1500. The current regulations specify that a label must conspicuously state, among other information:

1. The common or usual or chemical name of the hazardous ingredient(s);
2. The signal word “Danger” for products that are corrosive, extremely flammable, or highly toxic;
3. The signal word “Caution” or “Warning” for all other hazardous products
4. An affirmative statement of the principal hazard or hazards that the product presents, for example “Flammable”, “Harmful if Swallowed”, “Causes Burns”, “Vapor Harmful”, etc.;
5. Precautionary statements telling users what they must do or what actions they must avoid to protect themselves;
6. Where it is appropriate, instructions for first aid treatment to perform in the event that the product injures someone;
7. The word “Poison” for a product that is highly toxic, in addition to the signal word “Danger”;
8. The name and business address of manufacturer, packager, distributor or seller; and
9. The statement “Keep out of the reach of children”.

Additionally, a label writer considers MDI and its characteristics in relationship to the quantity of MDI in the product, likely exposure scenarios to MDI in the product, and the hazards posed by the product mixture, not just MDI, including any synergistic or antagonistic effects.

The responsibility for proper labeling rests with the manufacturer or distributor making a hazardous product available for consumers; however, help in preparing labels is available from a number of sources. For example, 16 C.F.R. 1500.128 states that a manufacturer may obtain informal comments on proposed labeling involving hazardous substances. Further information on the CPSC can be found on their website. Additionally, several industry trade associations provide labeling guidance to their member companies. See the "Websites and Resources" section in this document for more information.

Possible Health Hazards of MDI

An isocyanate is any chemical that contains at least one isocyanate functional group in its structure. An isocyanate group is one nitrogen atom attached by a double bond to one carbon atom that, in turn, is attached by a second double bond to an oxygen atom (-N=C=O). A chemical containing two such groups is called a diisocyanate. MDI is one such diisocyanate. Diphenylmethane diisocyanate, commonly referred to as MDI, is a white to yellowish solid at room temperature with no odor. Polymeric MDI, which is more commonly used, is a mixture of MDI monomer and oligomers. It is a brownish liquid at room temperature and may have a slight odor. A third type of MDI product, known commonly as "modified MDIs," are liquid at room temperature and are either colorless or slightly yellow.

Contact with excessive amounts of MDI vapor, liquid or aerosol can be harmful to human health. When handling MDI, there are four routes of exposure to consider:

- Inhalation,
- Eye contact,
- Skin contact, and
- Ingestion/swallowing.

Depending upon the concentration of MDI in the atmosphere, inhalation of airborne MDI may produce health effects such as irritation to the mucous membranes, the eyes, and the upper and lower respiratory tracts.

Inhalation of elevated levels of MDI also may result in the development of respiratory sensitization.

Exposures above occupational exposure limits(OELs) **(see Table 1)** may cause tearing and burning of the eyes, tightness of the chest, difficult or labored breathing, and more severe respiratory effects, including chemical bronchitis, pneumonitis, sensitization and pulmonary edema. Effects may be immediate and/or delayed for hours after exposure. Symptoms may increase or intensify for a few hours, but usually disappear within a day or two. However, both specific and non-specific bronchial responsiveness have in some cases persisted for months or even years.[1]

Exposure above workplace limits may lead to permanent pulmonary effects. Limited evidence from laboratory animals indicates that skin contact with MDI may play a role in respiratory sensitization. Sensitized individuals may experience severe asthma-like attacks whenever they are subsequently

exposed to even minute amounts of airborne diisocyanates. Asthma attacks can be life-threatening. Once sensitized, these individuals must avoid further exposure to diisocyanates.[2]

Table 1—Airborne Concentrations Standards/Guidelines*

OSHA	The Occupational Safety and Health Administration (OSHA) has set a Permissible Exposure Limit (Ceiling) [PEL(C)] for MDI in air of 20 parts per billion (ppb) (0.2 mg/m^3).
ACGIH	The American Conference of Governmental Industrial Hygienists (ACGIH) has adopted a Threshold Limit Value (TLV) of 5 ppb (0.051 mg/m^3) as an 8-hour Time Weighted Average (TWA).
CPSC	The Consumer Product Safety Commission has not established guidelines for MDI.

* Please read the latest version of the standards/guidelines, which provided on the supplier's safety data sheet (SDS), for updates.

Repeated or prolonged skin contact with liquid MDI may discolor the skin and cause redness, irritation, or swelling. Skin contact with MDI may also produce allergic contact dermatitis. If MDI comes into contact with the skin, the affected areas should be washed thoroughly with warm soapy water. Refer to the supplier SDS for specific recommendations.

Special Sensitization Concerns

1. Sensitization Reactions below Workplace Guidelines

MDI is a known skin and respiratory sensitizer. The ACGIH TLV for MDI is based, among other things, upon the potential for sensitization and is meant to protect workers from induction of this effect. However, there is no established level to which already sensitized individuals may be safely exposed. Therefore, previously sensitized individuals should avoid further exposure.[3]

2. Cross-Sensitization

Because there is some evidence of cross-sensitization among diisocyanates, individuals who have become sensitized to other diisocyanates should avoid exposure to MDI.[4]

Possible MDI Hazard Issues to Consider while Drafting Labeling

The most likely possible hazard issues for MDI are:

- Heating MDI-containing products or using them in a manner that causes MDI to become airborne may increase the potential for exposure. Exposure to elevated levels of airborne MDI may result in the development of respiratory sensitization.
- Skin contact with MDI can cause irritation. Skin contact with MDI also may result in dermal sensitization.
- Individuals already sensitized to MDI can have a skin or respiratory reaction from exposures to levels of diisocyanate below the OELs.
- Individuals already sensitized to another diisocyanate can have a skin or respiratory reaction from exposures to levels of MDI below the OELs.
- An individual with a pre-existing chronic asthma or skin condition can potentially have a reaction due to the irritant properties of MDI found at elevated airborne concentrations, or following direct skin contact.
- Although MDI has low oral toxicity, ingestion should be avoided. Further, ingestion may result in blockage of the digestive tract.*

***Note: The potential for blockage of the digestive tract after accidental ingestion by domestic animals has been reported. http://www.avma.org/onlnews/javma/oct06/061015n.asp**

Table 2 summarizes considerations relating to hazard issues and preventative measures for MDI. The information in Table 2 pertains to MDI, polymeric MDI and isocyanate terminated MDI prepolymer ingredients of consumer products that are not heated or sprayed. **For products where one or more of these MDI moieties is part of a mixture, the CPSC labeling standard requires that the hazards of the mixture, not its components, be discussed and recommends that the mixture itself should be tested.**

Table 2—MDI Labeling Considerations

Possible MDI Hazard/Property	Considerations
1. Respiratory irritant and sensitizer. Lung toxicity.	Inhalation exposure to airborne MDI at elevated concentrations has been shown to cause pulmonary sensitization, decrease of lung function, and reactive airways disease. Under the CPSC regulations, it is the responsibility of the manufacturer to determine the appropriate signal word and describe the primary hazard(s) on the main panel. 16 C.F.R. § 1500.121.
2. Skin and eye irritant and sensitizer.	Dermal effects include skin staining, irritation and potential allergic contact dermatitis (i.e., sensitization). Contact with the eye may cause eye irritation. Under the CPSC regulations, appropriate precautionary measures, such as PPE, must be

	placed on labels. 16 C.F.R. § 1500.121.
3. Evaporates very slowly at room temperature.	Use of products containing significant amounts of MDI monomer in very small, very poorly ventilated areas may result in measureable ambient MDI concentrations. Under the CPSC regulations, appropriate precautionary measures, such as adequate ventilation, must be placed on labels. 16 C.F.R. § 1500.121.
4. Sensitizer. Possible cross-sensitization with other isocyanates.	A person already sensitized to MDI or other diisocyanates can react (skin or respiratory) upon exposure to extremely low levels of exposure to MDI. There is also evidence that someone sensitized to one isocyanate may have a cross reactivity to another. According to ACGIH, for some sensitized individuals, avoiding exposure provides the only means to prevent the immune responses to sensitizing agents.[3]
5. Irritant properties.	At elevated airborne concentrations, respiratory irritants such as MDI may cause a reaction in individuals who have asthma or another pre-existing non-specific pulmonary hyperreactivity.
6. Moderate oral toxicity.	Although MDI is not highly toxic orally, it is not intended to be ingested. Further, ingestion may result in blockage of the digestive tract.*
7. Vapor pressure increases at higher temperatures.	Heating MDI-containing products may increase the amount of MDI in the air which increases the potential for inhalation exposure
8. Pulmonary irritation, sensitization, and lung function decrement.	Using MDI-containing products in a manner that causes MDI to become airborne, such as by spraying/heating, may allow MDI to be inhaled into the lungs, potentially causing respiratory effects.
9. Reaction with a small amount of water generates carbon dioxide.	If water reacts with MDI in a sealed container, the CO2 generated can cause swelling or rupturing of the container resulting in a possible spill or destruction of the container. This could be particularly important if containers are resealed and a product is contaminated with moisture.
10. Low volatility, skin effects.	Skin contact with MDI can cause localized discoloration or staining which is difficult to clean or remove. The use of appropriate skin protection (e.g., gloves) could reduce the potential for skin exposure. In the event of an accidental exposure, washing with soap and water is recommended.

*Note: The potential for blockage of the digestive tract after accidental ingestion by domestic animals has been reported. http://www.avma.org/onlnews/javma/oct06/061015n.asp

Useful Websites and Resources for Additional Guidance

Consumer Product Safety Commission webpage
www.cpsc.gov

CPSC regulations (Title 16 – Commercial Practices Chapter II – Consumer Product Safety Commission)
www.access.gpo.gov/nara/cfr/waisidx_03/16cfrv2_03.html

16 C.F.R. § 1500.128; guidance on CPSC Label Comment
http://ecfr.gpoaccess.gov/cgi/t/text/text-idx?c=ecfr&sid=021ca303bef0b3133291eea525c55250&rgn=div8&view=text&node=16:2.0.1.3.69.0.1.45&idno=16

American Society of Association Executives (ASAE) gateway listing of U.S. trade associations
http://www.asaecenter.org/Community/Directories/associationsearch.cfm

American Coatings Association (ACA)
http://www.paint.org/publications/labeling.html

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5. ACGIH. *TLVs*® and *BEIs*®, 2002 p. 7-8

Legal Notice

These Guidelines were prepared by the American Chemistry Council's Center for the Polyurethanes Industry. It is intended to provide general information to assist company label writers. It is not intended to serve as a substitute for in-depth training or labeling requirements, nor is it designed or intended to define or create legal rights or obligations. It is not intended to be a "how-to" manual, nor is it a prescriptive guide. All persons who may be responsible for communicating the potential hazards and safe handling guidelines for consumer products and to prospective customers have an independent obligation to ascertain that their actions are in compliance with current federal, state and local laws and regulations and should consult with legal counsel concerning such matters. These guidelines are necessarily general in nature and individual companies may vary their approach with respect to particular practices based on specific factual circumstance, the practicality and effectiveness of particular actions and economic and technological feasibility. Any mention of specific products in these guidelines are for illustration purposes only and is not intended as a recommendation or endorsement of such products. Items in this document may be trademarked, which may or may not be noted in this document. Neither the American Chemistry Council, nor the individual member companies of the Center for the Polyurethanes Industry of the American Chemistry Council, nor any of their respective directors, officers, employees, subcontractors, consultants, or other assigns, makes any warranty or representation, either express or implied, with respect to the accuracy or completeness of the information contained in this manual; nor do the American Chemistry Council or any member companies assume any liability or responsibility for any use or misuse, or the results of such use or misuse, of any information, procedure, conclusion, opinion, product, or process disclosed in these Guidelines. NO WARRANTIES ARE GIVEN; ALL IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE ARE EXPRESSLY EXCLUDED.

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